

# Iron isotopes in deep sea hydrothermal vents: The iron flux to the deep ocean and its importance to the global iron cycle

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Motivation for this project stems from recent interest in the global geochemical cycle of iron, due to revelations that fertilization of the surface ocean with iron may affect global climate, (i.e. Peng and Broecker, 1991). While iron fertilization of high-nutrient, low-chlorophyll (HNLC) regions of the world's oceans such as the Southern Ocean and the equatorial Pacific Ocean may drawdown atmospheric CO<sub>2</sub> on short timescales (Cooper et al., 1996), it is unknown how fertilization will affect global climate over long timescales (Charette and Buesseler, 2000; Ridgwell, 2000). Of primary importance to this debate is the question of which iron sources are most important to open ocean ecosystems and which would be primarily responsible for natural iron fertilization.

**Table 1– Iron fluxes to the surface ocean. Compiled from (Coale et al., 1996) and (Fung et al., 2000).**

Parameter	Flux (nmol m <sup>-2</sup> d <sup>-1</sup> )	Data Source
Iron Source		
Upwelling	120 14	(Coale et al., 1996) (Fung et al., 2000)
Diffusion	0.20 (tied to upwelling)	(Coale et al., 1996) (Fung et al., 2000)
Atmospheric	5 to 25 173	(Coale et al., 1996) (Fung et al., 2000)
Total	125.2 to 145.2 ~187	(Coale et al., 1996) (Fung et al., 2000)
C:Fe phytoplankton	167,000 mol:1 mol	(Coale et al., 1996)
C:Fe cell	400,000 mol:1 mol	(Fung et al., 2000)
% nitrate available	~80% ~98%	(Coale et al., 1996) (Fung et al., 2000)

Coale et al. (1996): equatorial Pacific Ocean at 140°W; 120 m thick euphotic zone; directly-measured data

Fung et al. (2000): data for equatorial Pacific Ocean (subset of total data); remotely-sensed data

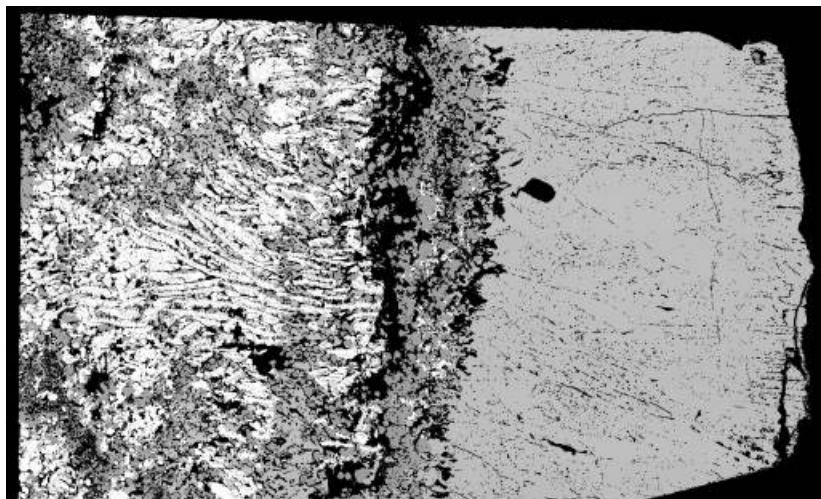
Of the possible sources of iron to HNLC regions of the global ocean, most attention has been paid to dust (Fung et al., 2000; Watson, 1997) and continental slope sediment-derived iron (Coale et al., 1996; Table 1). However, riverine iron and deep sea hydrothermal iron both constitute viable iron sources over geologic timescales. Two crucial issues in this debate, those of the immediate and ultimate sources of the iron to fertilized regions of the surface ocean, are thus far unresolved.

In order to understand the variance of deep ocean iron input and the importance of this source to fertilization, and thus global climate, the current work

uses elemental and isotopic data to study hydrothermal iron from a deep sea chimney.

To this end we have initiated a study of the elemental composition and iron isotopic composition of the deep sea hydrothermal chimney Finn from the Mothra vent field (Endeavour segment of the Juan de Fuca ridge). A cross-section of the chimney sample, approximately 6.4 cm in length and illustrated in the backscattered electron (BSE) image below (Figure 1), reveals three major

sulfide mineral phases. Reflected light microscopy indicates that the inner wall vent-chimney interface (302°C vent fluid) is composed of ~ 1.2 cm of massive chalcopyrite ( $\text{CuFeS}_2$ ), succeeded by various intergrowths of sub- to euhedral pyrite ( $\text{FeS}_2$ ), chalcopyrite, and sphalerite ( $\text{ZnS}$ ). The outermost section of the chimney, in contact with 2°C seawater, is dominated by euhedral to subhedral sphalerite and minor amounts of pyrite. Minor barite and anhydrite are also present throughout the section.



**Figure 1 – False color backscattered electron (BSE) image of one half of the Finn cross-section, from the inner conduit interface of massive chalcopyrite (right) towards the outer, seawater interface dominated by sphalerite (left). Darker gray colors represent sub- to euhedral pyrite while the lighter gray and white represent chalcopyrite and sphalerite, respectively. The half cross-section is approximately 3.0 cm in length.**

The relative abundances of seventeen elements are being determined using a Cameca SX-51 electron microprobe, with a typical analytical accuracy of 1 - 5 % for major and minor elements. The elements under consideration in this study are the transition metals Cu, Co, Cr, Fe, Mn, Mo, Ni, Ti, Zn, as well as Al, Ba, Ca, Mg, Na, O, S, and Si. Preliminary results suggest variation in major elements such as Fe, Cu, and Zn between the inner conduit and outer interface. Sphalerites measured from the inner conduit to the outer interface range in Fe composition from 1.1 to 13.4%, with an average of 6.5% over 1001 separate point analyses. Zinc in these same sphalerites varies between 48.5 and 65.5% (59.6% average) while sulfur exhibits a much narrower range between 30.7 and 36.3% (32.7% average). In contrast, the massive chalcopyrite at the inner conduit interface exhibits small variations in both Fe and Cu compositions (29.3 to 31.1% and 29.9 to 33.7%, respectively).

Iron isotopic compositions are being measured on a VG Sector 54 thermal-ionization multi-collector mass spectrometer, using a 54-58 double spike technique similar to that described by (Johnson and Beard, 1999). Samples from the chimney Finn are extracted with an automated Merchantek Micromilling microscale sampling system, capable of sampling at a spatial resolution of up to twenty-five microns. Typically, about one hundred to two hundred milligrams of sphalerite, pyrite, and chalcopyrite are extracted and subjected to chemical purification, consisting of hydrofluoric/perchloric acid digestion of the sample, and iron separation from the matrix via ion exchange chromatography. The eluted iron is suspended in 0.5N  $\text{HNO}_3$  solution and ~4µg are loaded onto a rhenium filament with high-purity aluminum oxide, phosphoric acid, and silica gel.

Thus far, we have completed iron isotope analyses of our standards, single and double spikes, and spiked standards, in order to calibrate the double spike technique and derive a spike

subtraction scheme. Work has also been done to calibrate the ion exchange chromatography and test iron yields. Initial indications are that iron isotope compositions can be measured to  $\sim 0.3\%$  external precision for  $\delta^{56}\text{Fe}$ . By far the largest source of error in the data, which is then translated to calculation of the sample  $\delta^{56}\text{Fe}$ , is laboratory contamination in the measurement of the 54-58 double spikes. This analytical precision is acceptable, in light of Polizzotto et al.'s (2000) analyses of hydrothermal fluids from low-Mg, high temperature vents along the Juan de Fuca ridge. These authors find the vent fluid to be isotopically light ( $-0.7$  to  $-1.2\%$ ), values that would fall well outside the envelope of analytical uncertainty expected from our measurements of iron thus far.

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